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**EP-A- 0 261 988**

Die Makromolekulare Chemie vol. 184, no. 9,  
September 1983, pages 1861-1867, Huethig &  
Wepf Verlag, Basel, CH; G. DACCORD et al.:  
"Oligo(thiophénylènes-1,4) alpha, omega-  
difonctionnalisés" \* page 1862, formula 7 \*

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## Description

This invention relates to a novel aromatic sulfideamide polymer and a process for production of the novel polymer. The polymers according to the invention have a chemical structure in which phenylene and alkylene groups are alternately bonded via an amide group and a thioether group. The polymers are useful as materials for producing articles exhibiting improved properties such as excellent resistance to high temperatures, flame-retardant properties, resistance to solvents, good mechanical properties, etc.

Polyphenylene sulfide which is a polymeric compound comprising phenylene groups linked to each other via a thioether group is well known in the art. This polymer has such properties as good flame-retardancy, low moisture absorption, high dimensional stability, etc. However, since this type of polymer exhibits a relatively low heat distortion temperature (HDT) of 260 °C (GF 40%; i.e. where containing 40% by weight of glass fibers) and a crystalline melting point of 281 °C, its usefulness in applications where high resistance to heat is required is inevitably limited. Consequently there has been a demand in the art for the development of polyphenylene sulfide materials having higher crystalline melting points.

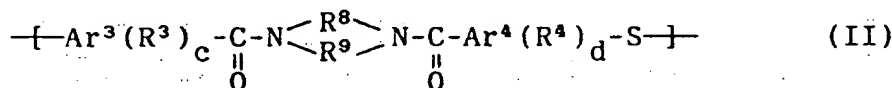
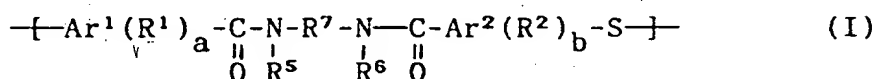
A polymer substance containing thioether, phenylene and amide groups in the macromolecular backbone, i.e. a polymer of aromatic polythioether amide, and a process for production thereof are described in JP-A-60-226528. This polymer substance presents some problems in practice because it has a rather low softening point, is soluble in organic solvents such as dimethyl sulfoxide or N-methyl-2-pyrrolidone and exhibits poor resistance to chemicals. Additionally the synthesis of thiol group-containing monomers to be used in the preparation of the polymer is so expensive that production of the polymer is not feasible from an economic point of view.

Aromatic sulfideamide polymers derived from aliphatic dicarboxylic acids and aromatic amines are described by G. Daccord and B. Sillion in *Die Makromolekulare Chemie*, 1983, 184, p. 1861 ff. These polymers melt at relatively low temperatures.

An object of the present invention, therefore, is to provide a novel aromatic sulfideamide polymer substance comprising a commercially available, inexpensive aliphatic moiety in the repeating units and which is improved in terms of resistance to high temperatures, resistance to solvents and mechanical properties.

A further object of the present invention is to provide a process for production of such a novel polymer substance.

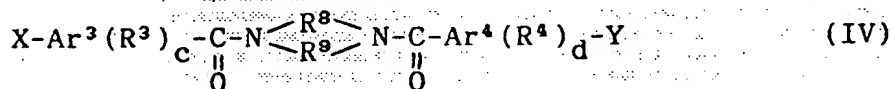
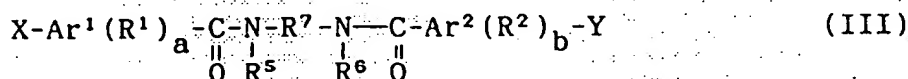
According to one aspect of the present invention, there is provided an aromatic sulfideamide polymer which comprises repeating structural units represented by the following formula (I) and/or (II):



wherein Ar<sup>1</sup>, Ar<sup>2</sup>, Ar<sup>3</sup> and Ar<sup>4</sup> each represent an aromatic ring; R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup>, R<sup>4</sup>, R<sup>5</sup> and R<sup>6</sup>, which may be the same or different, each represent an alkyl group having 1 to 20 carbon atoms, a cycloalkyl group having 3 to 20 carbon atoms, an aryl group having 6 to 20 carbon atoms, an alkoxy group having 1 to 20 carbon atoms, an acyl group having 2 to 20 carbon atoms or an arylalkyl group having 7 to 20 carbon atoms, each of R<sup>5</sup> and R<sup>6</sup> optionally being hydrogen; a, b, c and d, which may be the same or different, each represent an integer of from 0 to 4; and R<sup>7</sup>, R<sup>8</sup> and R<sup>9</sup>, which may be the same or different, each represent an alkylene group having 1 to 20 carbon atoms, said polymer preferably having a logarithmic viscosity [η] of 0.02 to 2.00, as determined by measuring the relative viscosity of polymer dissolved in concentrated sulfuric acid (specific gravity of 1.84) at 30 °C and at a polymer concentration of 0.5 g/100 ml and computing the result in accordance with the equation:

$$[\eta] = \ln \frac{(\text{relative viscosity})}{(\text{polymer concentration})}$$

According to another aspect of the present invention, there is provided a process for production of an aromatic sulfideamide polymer comprising the above defined repeating units (I) and/or (II) [in which the ratio of units (I) to units (II) ranges from 100:0 to 0:100]; said process comprising the step of sulfidizing one or more amide group-containing dihalide compounds having the following general formula (III) and/or (IV) with a sulfidizing agent in an organic polar solvent;

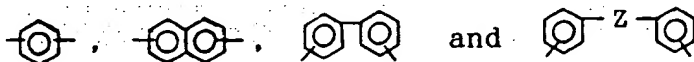


wherein Ar<sup>1</sup>, Ar<sup>2</sup>, Ar<sup>3</sup> and Ar<sup>4</sup> each represent an aromatic ring; R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup>, R<sup>4</sup>, R<sup>5</sup> and R<sup>6</sup>, which may be the same or different, each represent an alkyl group having 1 to 20 carbon atoms, a cycloalkyl group having 3 to 20 carbon atoms, an aryl group having 6 to 20 carbon atoms, an alkoxy group having 1 to 20 carbon atoms, an acyl group having 2 to 20 carbon atoms or an arylalkyl group having 7 to 20 carbon atoms, each of R<sup>5</sup> and R<sup>6</sup> optionally being hydrogen; a, b, c and d, which may be the same or different, each represent an integer of from 0 to 4; R<sup>7</sup>, R<sup>8</sup> and R<sup>9</sup>, which may be the same or different, each represent an alkylene group having 1 to 20 carbon atoms; and X and Y, which may be the same or different, each represent a halogen.

The accompanying Figs. 1 and 2 shown an IR spectrum (wave length: 400 - 4000 cm<sup>-1</sup>) and an X-ray diffraction pattern (X-ray intensity: counts/angle: 10° - 40°) of the polymer obtained in Example 1, respectively.

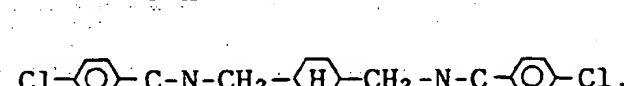
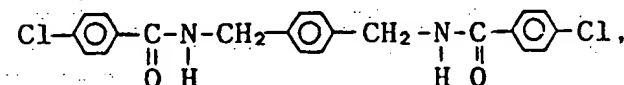
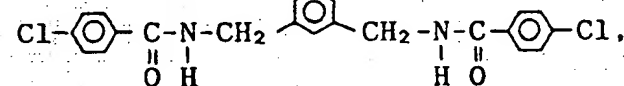
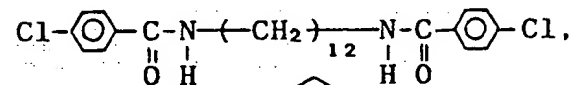
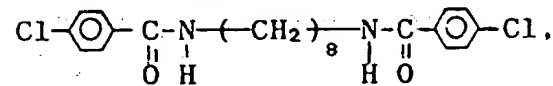
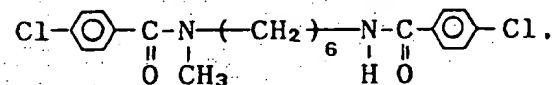
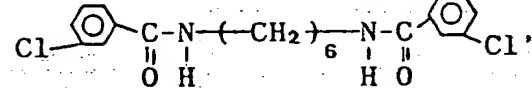
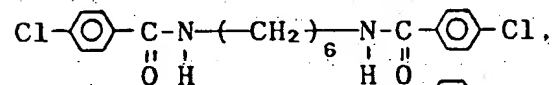
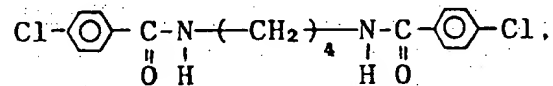
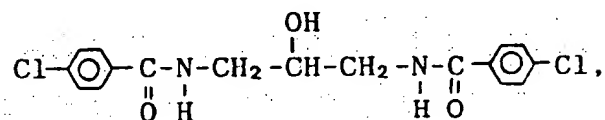
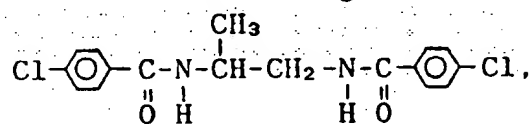
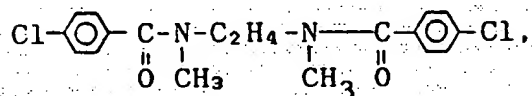
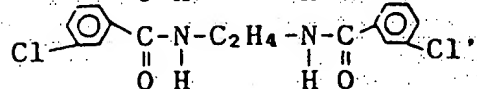
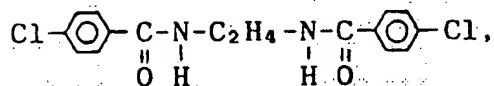
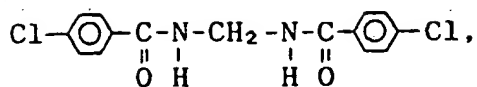
The invention will now be described in more detail.

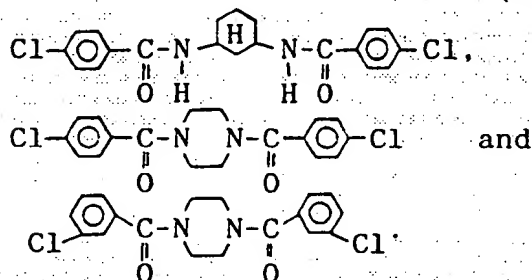
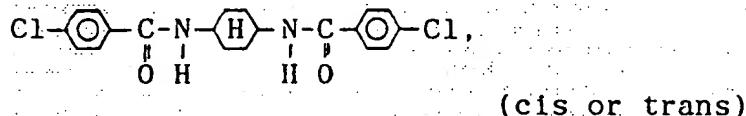
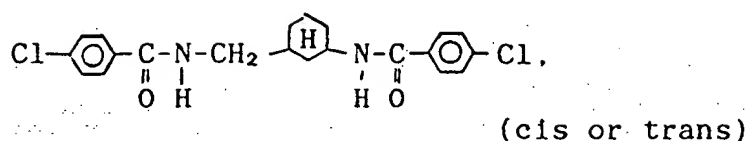
Examples of groups Ar<sup>1</sup>, Ar<sup>2</sup>, Ar<sup>3</sup> and Ar<sup>4</sup> in the amide group-containing dihalide compounds which may be used in the invention include:



where Z represents -O-, -S-, -SO<sub>2</sub>-, -CO-, -CH<sub>2</sub>- or -C(CH<sub>3</sub>)<sub>2</sub>-. The groups may be the same or different in one compound.

Examples of particularly preferred dihalide compounds (III) and (IV) for use in the present invention include:





It is preferred that the amide group-containing dihalide compounds contain bonds at the para positions if it is mainly desired to improve the thermal resistance properties of the product polymers. On the other hand, if it is desired to improve the solubility and molding properties of the sulfideamide polymer products, the dihalide compounds may contain bonds at the meta positions and/or at the ortho positions, or may be branched.

The amide group-containing dihalide compounds may be synthesized by the conventional amide linkage formation technique. A typical example of synthesis is a process in which a corresponding halogen-containing aromatic carbonyl chloride is reacted with a corresponding aliphatic diamine.

The organic polar solvents used in the process of the present invention are preferably aprotic ones and ones which are stable in the presence of alkalis at elevated temperatures. Examples of the preferred solvents include N,N-dimethyl acetamide (DMA), N-ethyl-2-pyrrolidone, hexamethyl phosphoric triamide (HMPA), dimethyl sulfoxide (DMSO), N-methyl-2-pyrrolidone (NMP), 1,3-dimethyl imidazolidinone.

The sulfidizing agents which may be used in the process include alkali metal sulfides, combinations of hydrogen sulfide with alkali metal bases, and combinations of alkali metal hydrosulfides with alkali metal basis. The alkali metal sulfides and hydrosulfides may be used as hydrates (from 0.5 to 10 molar equivalents). The sulfidizing agents may be prepared in situ prior to introduction of the dihalide compound of the general formula (III) and/or (IV) into the reaction system. Of course, the sulfidizing agent may be prepared outside the reaction system and then introduced to the system. It is preferred that, before the sulfidizing agent is introduced for commencement of the polymerization in the reaction system, the content of water in the system should be reduced to a level of less than 2.5 molar equivalents per equivalent of the sulfidizing agent to be introduced.

Among the available sulfidizing agents, sodium sulfide, sodium hydrosulfide in conjunction with sodium hydroxide, and hydrogen sulfide in conjunction with sodium hydroxide are preferred.

In the polymerization, a phase transfer catalyst such as a crown-ether compound, phosphor salt or an ammonium salt compound and/or as an assistant such as an alkali metal carboxylate may be used to effectively increase the molecular weight of the resulting polymer.

The polymerization is effected at a temperature of about 150 - 300 °C, preferably 180 - 280 °C, for a period of about 0.5 - 24 hours, preferably 1 - 12 hours.

The preferred molar ratio of the dihalide compound (III) and/or (IV) to the sulfidizing agent used in the present process ranges from 0.9:1.0 to 1.1:1.0.

The quantity of solvent used in the process may be such that the reaction system will contain 7 - 50%, preferably 10 - 40%, by weight of the product polymer upon completion of the polymerization.

The process may comprise the further step of recovering the polymer e.g. by conventional methods, such as vacuum, solvents or water. The isolated product polymer may be washed with any suitable organic solvent or water and then dried.

Generally, the aromatic sulfideamide polymers according to the present invention have a logarithmic viscosity in the range of 0.02 to 2.00, as measured at a concentration of 0.5 g/100 ml in concentrated sulfuric acid at a temperature of 30 °C. Polymers having viscosities of 0.05 to 2.00 are preferred.

The aromatic polysulfideamide polymers of the invention may be advantageously chain-extended and/or cross-linked and/or branched by heating in an oxidative atmosphere, such as air or oxygen-enriched air.

Where the polymers are molded or otherwise shaped, they may contain various filler materials. Examples of suitable filler materials include (a) fiber fillers, such as glass fibers, carbon fibers, boron fibers, aramid fibers, alumina fibers, etc. and (b) inorganic fillers, such as mica, talc, clay, graphite, carbon black, silica, asbestos, molybdenum disulfide, magnesium oxide, calcium oxide, etc.

As shown in the following Examples, the polymers of the present invention exhibit, on IR analysis, absorptions around  $1090\text{ cm}^{-1}$  (caused by thioether linkages), around  $1640\text{ cm}^{-1}$  (caused by carbonyl groups in amide linkages) and around  $3320\text{ cm}^{-1}$  and  $1540\text{ cm}^{-1}$  (both caused by amino groups in amide linkages). These IR data confirm that the present polymers have the structural repeating units (I) and/or (II).

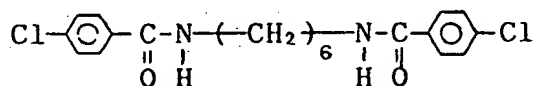
The invention is illustrated in detail by the following Examples.

Since most of the polymers according to the invention are only soluble in some special solvents such as concentrated sulfuric acid or an N-methyl-2-pyrrolidone/lithium chloride (95/5 by weight) mixture, and are only sparingly soluble or insoluble in common organic solvents, it is not readily possible to determine the average molecular weight of the present polymers by a conventional method. Hence, the logarithmic viscosity value  $[\eta]$  of a polymer is herein employed as a measure of the molecular weight of that polymer. The logarithmic viscosity value  $[\eta]$  is obtained by measuring the relative viscosity of polymer dissolved in a concentrated sulfuric acid solvent at  $30^\circ\text{C}$  and at a polymer concentration of  $0.5\text{ g}/100\text{ ml}$  and calculating the result in accordance with the equation:

$$[\eta] = \ln \frac{(\text{relative viscosity})}{(\text{polymer concentration})}$$

#### Example 1

A 500 ml autoclave was charged with  $\text{Na}_2\text{S} \cdot 2.7\text{H}_2\text{O}$  (0.04 moles) and N-methyl-2-pyrrolidone (NMP) 150 ml and heated to a temperature of  $200^\circ\text{C}$  with stirring so as to dehydrate the mixture. By this dehydration, 1.26 g of water containing 4.31% of NMP was distilled off. After cooling the reaction system down to  $100^\circ\text{C}$ , a dichloride.



(0.04 moles) was added together with an additional 50 ml of NMP. The system was shielded and heated to  $250^\circ\text{C}$ . At this temperature, the polymerization was allowed to proceed for 6 hours.

At the end of the polymerization period, the system was cooled and methanol was added to precipitate out the product polymer. The mixture was filtered. The filter cake was repeatedly washed with warm water and filtered and then washed with methanol and dried to give a light gray powdery polymer product (10 g; corresponding to a yield of 70.6%).

The polymer had a logarithmic viscosity of 0.16 (as measured in  $\text{H}_2\text{SO}_4$  at a concentration of  $0.5\text{ g}/100\text{ ml}$  at  $30^\circ\text{C}$ ). The polymer as such was not melt-moldable, but was soluble in, for example, concentrated sulfuric acid or NMP/LiCl mixture (such a solution could be used in casting to give a film).

The infra-red absorption spectrum of the polymer showed absorptions at  $1090\text{ cm}^{-1}$  (thioether linkage) and  $3350$ ,  $1640$  and  $1544\text{ cm}^{-1}$  (amide linkage, respectively) (see Fig. 1).

Results of the elemental analysis are listed below:

Found (wt%):	C	66.9,	H	5.8,	N	7.7,	S	8.6
Theoretical (wt%):	C	67.8,	H	6.2,	N	7.9,	S	9.0

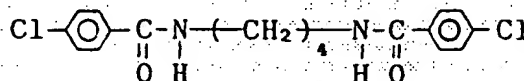
X-ray diffraction confirmed that the product sulfideamide polymer was crystalline in nature (see Fig. 2). The polymer showed a decomposition temperature of  $425^\circ\text{C}$  but did not show a definite melting point.

Examples 2 - 7

The apparatus and procedure of Example 1 was used to polymerize various dihalide compounds. The polymers obtained in all the cases were crystalline.

Example 2

The following dihalide compound was employed:



Yield: 11.4 g (87.3%)

Logarithmic viscosity: 0.11 (measured with a 0.5 g/100 ml solution in  $\text{H}_2\text{SO}_4$  at  $30^\circ\text{C}$ )

IR:  $1090\text{ cm}^{-1}$  (thioether linkage)  $3320$ ;  $1617$ ;  $1541\text{ cm}^{-1}$  (amide linkage)

## Elemental analysis:

Found (wt%):	C	65.5,	H	5.4,	N	8.3,	S	8.8
Theoretical (wt%):	C	66.2,	H	5.5,	N	8.6,	S	9.8

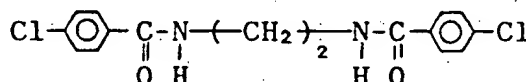
Decomposition temperature:  $413^\circ\text{C}$  (with no definite melting point)

Soluble in concentrated sulfuric acid, NMP/LiCl mixture.

Insoluble in methanol, DMF, DMSO, NMP.

Example 3

The following dihalide compound was employed:



Yield: 9.7 g (81.3%)

Logarithmic viscosity: 0.08 (measured with a 0.5 g/100 ml solution in  $\text{H}_2\text{SO}_4$  at  $30^\circ\text{C}$ )

IR:  $1070\text{ cm}^{-1}$  (thioether linkage),  $3320$ ;  $1642$ ;  $1552\text{ cm}^{-1}$  (amide linkage)

## Elemental analysis:

Found (wt%):	C	64.0,	H	4.6,	N	9.2,	S	8.9
Theoretical (wt%):	C	64.4,	H	4.7,	N	9.4,	S	10.7

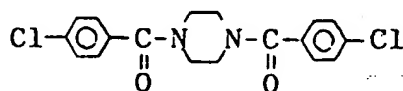
Decomposition temperature:  $351^\circ\text{C}$  (with no definite melting point)

Soluble in concentrated sulfuric acid, NMP/LiCl mixture.

Insoluble in methanol, DMF, DMSO.

Example 4

The following dihalide compound was employed:



Yield: 10.4 g (80.1%)

Logarithmic viscosity: 0.10 (measured with a 0.5 g/100 ml solution in H<sub>2</sub>SO<sub>4</sub> at 30 °C)

IR: 1075 cm<sup>-1</sup> (thioether linkage), 1642 cm<sup>-1</sup> (carbonyl group)

Elemental analysis:

Found (wt%):	C	65.0,	H	4.9,	N	8.5,	S	8.1
Theoretical (wt%):	C	66.7,	H	5.0,	N	8.6,	S	9.9

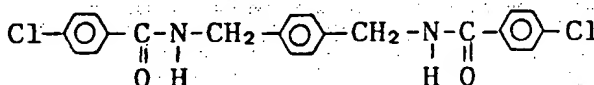
Decomposition temperature: 432 °C (with no definite melting point)

Soluble in concentrated sulfuric acid, NMP/LiCl mixture.

Insoluble in methanol, DMF, DMSO.

Example 5

The following dihalide compound was employed:



Yield: 14.6 g (97.9%)

Logarithmic viscosity: 0.09 (measured with a 0.5 g/100 ml solution in H<sub>2</sub>SO<sub>4</sub> at 30 °C)

IR: 1090 cm<sup>-1</sup> (thioether linkage), 3320; 1642; 1542 cm<sup>-1</sup> (amide linkage)

Elemental analysis:

Found (wt%):	C	68.9,	H	4.8,	N	7.3,	S	7.7
Theoretical (wt%):	C	70.1,	H	4.8,	N	7.5,	S	8.5

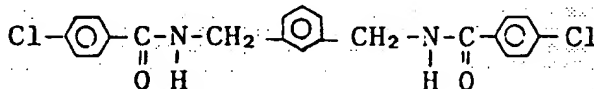
Decomposition temperature: 384 °C (with no definite melting point)

Soluble in concentrated sulfuric acid, NMP/LiCl mixture.

Insoluble in methanol, DMF, DMSO.

Example 6

The following dihalide compound was employed:



Yield: 14.9 g (99.0%)

Logarithmic viscosity: 0.09 (measured with a 0.5 g/100 ml solution in H<sub>2</sub>SO<sub>4</sub> at 30 °C)

IR: 1080 cm<sup>-1</sup> (thioether linkage), 3300; 1640; 1542 cm<sup>-1</sup> (amide linkage)

Elemental analysis:

Found (wt%):	C	69.6,	H	4.7,	N	7.3,	S	8.0
Theoretical (wt%):	C	70.1,	H	4.8,	N	7.5,	S	8.5

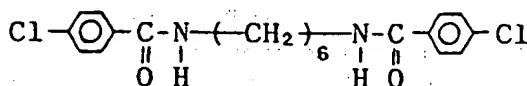
Decomposition temperature: 387 °C (with no definite melting point)

Soluble in concentrated sulfuric acid, NMP/LiCl mixture, NMP, DMSO, DMA.

Insoluble in methanol, m-cresol, pyridine.

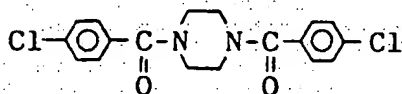
## Example 7

The following dihalide compounds were employed in admixture:



(0.02 moles)

and



(0.02 moles)

Yield: 11.2 g (82.3%)

Logarithmic viscosity: 0.11 (measured with a 0.5 g/100 ml solution in H<sub>2</sub>SO<sub>4</sub> at 30°C)

IR: 1080 cm<sup>-1</sup> (thioether linkage), 3350; 1642; 1545 cm<sup>-1</sup> (amide linkage)

Elemental analysis:								
Found (wt%):	C	66.9,	H	5.5,	N	8.3,	S	9.1
Theoretical (wt%):	C	67.2,	H	5.6,	N	8.3,	S	9.5

Found (wt%):	C	66.9,	H	5.5,	N	8.3,	S	9.1
Theoretical (wt%):	C	67.2,	H	5.6,	N	8.3,	S	9.5

Decomposition temperature: 427°C (with no definite melting point)

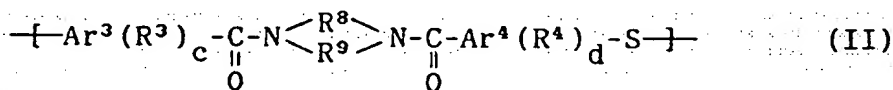
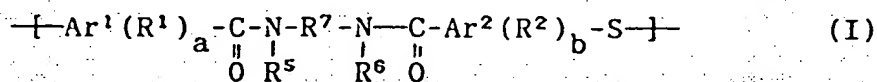
Soluble in concentrated sulfuric acid, NMP/LiCl mixture.

Insoluble in methanol, DMF.

From the above description, it will be appreciated that the present invention provides a novel class of aromatic sulfideamide polymers which may be synthesized from commercially available materials by a simple process. It is expected that the polymers will find a wide range of applications as engineering plastics because of their excellent heat resistance properties and processability.

### Claims

1. An aromatic sulfideamide polymer which comprises repeating structural units represented by the following formula (I) and/or (II):



wherein Ar<sup>1</sup>, Ar<sup>2</sup>, Ar<sup>3</sup> and Ar<sup>4</sup> each represent an aromatic ring; R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup>, R<sup>4</sup>, R<sup>5</sup> and R<sup>6</sup>, which may be the same or different, each represent an alkyl group having 1 to 20 carbon atoms, a cycloalkyl group having 3 to 20 carbon atoms, an aryl group having 6 to 20 carbon atoms, an alkoxy group having 1 to 20 carbon atoms, an acyl group having 2 to 20 carbon atoms or an arylalkyl group having 7 to 20 carbon atoms, each of R<sup>5</sup> and R<sup>6</sup> optionally being hydrogen; a, b, c and d, which may be the same or different, each represent an integer of from 0 to 4; and R<sup>7</sup>, R<sup>8</sup> and R<sup>9</sup>, which may be the same or different, each represent an alkylene group having 1 to 20 carbon atoms.

2. A polymer as claimed in Claim 1 in which groups Ar<sup>1</sup>, Ar<sup>2</sup>, Ar<sup>3</sup> and Ar<sup>4</sup> are each selected from

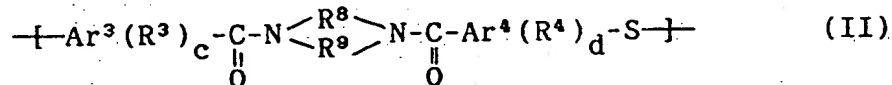
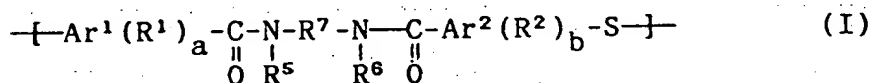


where Z represents -O-, -S-, -SO<sub>2</sub>-, -CO-, -CH<sub>2</sub>- or -C(CH<sub>3</sub>)<sub>2</sub>-.

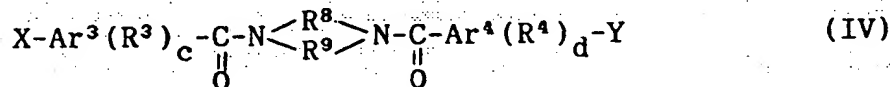
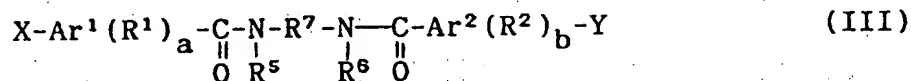
3. A polymer as claimed in Claim 1 or Claim 2 which has a logarithmic viscosity  $[\eta]$  of 0.02 to 2.00, preferably 0.05 to 2.0 as determined by measuring the relative viscosity of polymer dissolved in concentrated sulfuric acid at 30 °C and at a polymer concentration of 0.5 g/100 ml and computing the result in accordance with the equation:

$$[\eta] = \ln \frac{(\text{relative viscosity})}{(\text{polymer concentration})}$$

4. A polymer as claimed in Claims 1 to 3 which has been chain-extended and/or cross-linked and/or branched by heating in an oxidative atmosphere.
5. A process for production of an aromatic sulfideamide polymer comprising repeating units represented by the following formula (I) and/or (II):

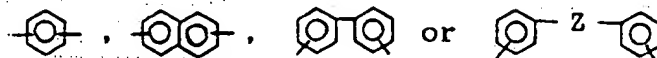


said process comprising the step of sulfidizing one or more amide group-containing dihalide compounds having the following general formula (III) and/or (IV) with a sulfidizing agent in an organic polar solvent:



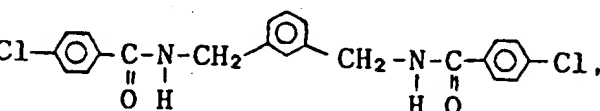
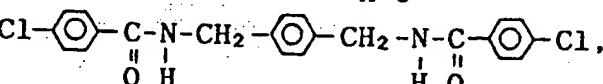
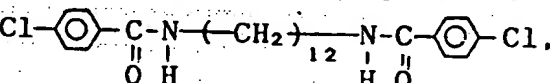
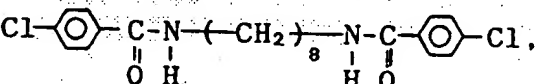
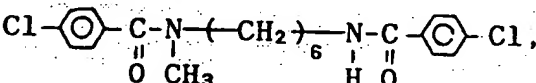
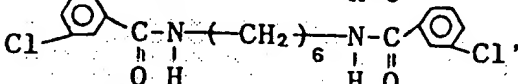
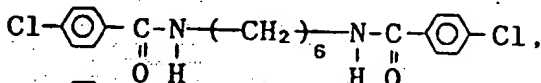
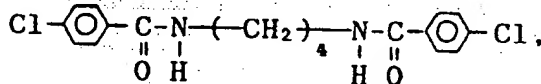
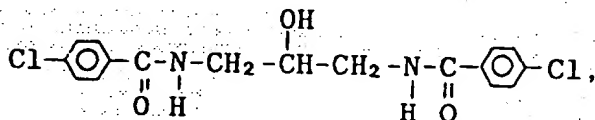
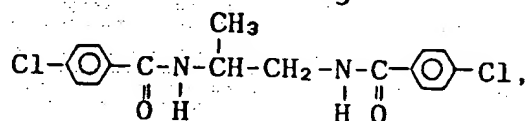
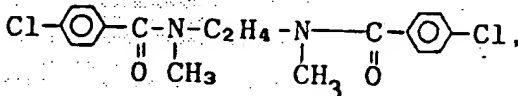
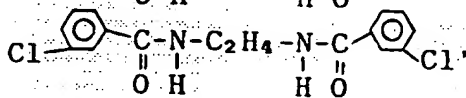
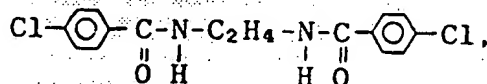
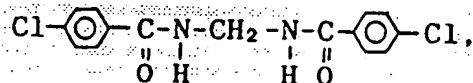
wherein Ar<sup>1</sup>, Ar<sup>2</sup>, Ar<sup>3</sup> and Ar<sup>4</sup> each represent an aromatic ring; R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup>, R<sup>4</sup>, R<sup>5</sup> and R<sup>6</sup>, which may be the same or different, each represent an alkyl group having 1 to 20 carbon atoms, a cycloalkyl group having 3 to 20 carbon atoms, an aryl group having 6 to 20 carbon atoms, an alkoxy group having 1 to 20 carbon atoms, an acyl group having 2 to 20 carbon atoms or an arylalkyl group having 7 to 20 carbon atoms, each of R<sup>5</sup> and R<sup>6</sup> optionally being hydrogen; a, b, c and d, which may be the same or different, each represent an integer of from 0 to 4; R<sup>7</sup>, R<sup>8</sup> and R<sup>9</sup>, which may be the same or different, each represent an alkylene group having 1 to 20 carbon atoms; and X and Y, which may be the same or different, each represent a halogen.

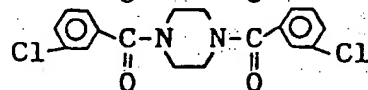
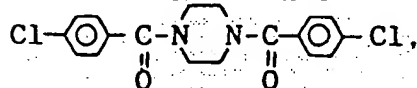
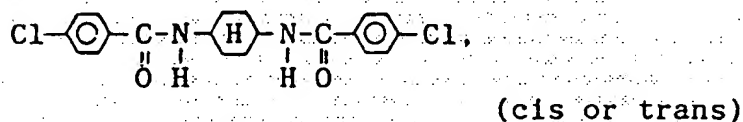
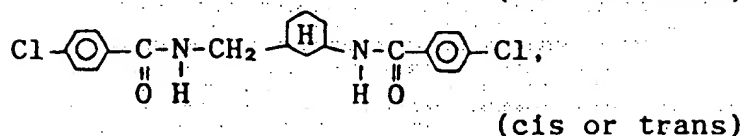
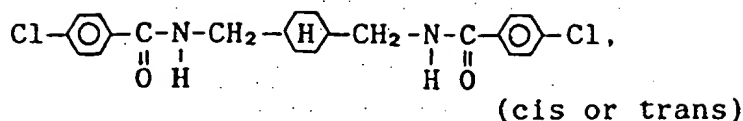
6. A process as claimed in Claim 5 in which groups Ar<sup>1</sup>, Ar<sup>2</sup>, Ar<sup>3</sup> and Ar<sup>4</sup> are each selected from



where Z represents -O-, -S-, -SO<sub>2</sub>-, -CO-, -CH<sub>2</sub>- or -C(CH<sub>3</sub>)<sub>2</sub>-.

7. A process as claimed in Claim 5 or Claim 6 in which the amide group-containing dihalide compound employed is selected from the group consisting of:





and mixtures thereof.

8. A process as claimed in Claim 5, 6 or 7 in which the organic solvent is aprotic.

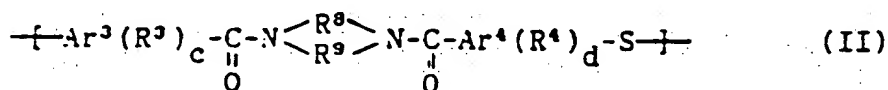
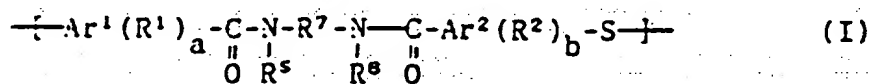
9. A process as claimed in Claim 8 in which the solvent is selected from N,N-dimethyl acetamide, N-ethyl-2-pyrrolidone, hexamethyl phosphoric triamide, dimethyl-sulfoxide, N-methyl-2-pyrrolidone, and 1,3-dimethyl imidazoline.

10. A process as claimed in Claim 5, 6, 7, 8 or 9 in which the sulfidizing agent is selected from sodium sulfide, a combination of sodium hydrosulfide and sodium hydroxide, and a combination of hydrogen sulfide and sodium hydroxide.

11. A composition comprising an aromatic sulfideamide polymer as claimed in Claim 1, 2, 3 or 4 or produced by a process claimed in any one of Claims 5 to 10 and one or more conventional additives.

#### Patentansprüche

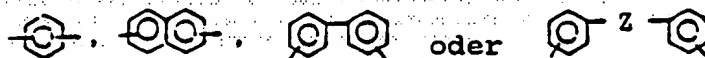
1. Aromatisches Sulfid-Amid-Polymer, welches wiederkehrende Struktureinheiten umfaßt, die durch die folgende Formel (I) und/oder (II) dargestellt sind:



worin  $\text{Ar}^1$ ,  $\text{Ar}^2$ ,  $\text{Ar}^3$  und  $\text{Ar}^4$  jeweils einen aromatischen Ring bedeuten;  $\text{R}^1$ ,  $\text{R}^2$ ,  $\text{R}^3$ ,  $\text{R}^4$ ,  $\text{R}^5$  und  $\text{R}^6$ , die gleich oder voneinander verschieden sein können, jeweils eine Alkylgruppe mit 1 bis 20 Kohlenstoffatomen, eine Cycloalkylgruppe mit 3 bis 20 Kohlenstoffatomen, eine Arylgruppe mit 6 bis 20 Kohlenstoffatomen, eine Alkoxygruppe mit 1 bis 20 Kohlenstoffatomen, eine Acylgruppe mit 2 bis 20 Kohlenstoffatomen oder eine Arylalkylgruppe mit 7 bis 20 Kohlenstoffatomen bedeuten, wobei  $\text{R}^5$  und  $\text{R}^6$  jeweils

wahlweise Wasserstoff sind; a, b, c und d, die gleich oder voneinander verschieden sein können, jeweils eine ganze Zahl von 0 bis 4 bedeuten; und R<sup>7</sup>, R<sup>8</sup> und R<sup>9</sup>, die gleich oder voneinander verschieden sein können, jeweils eine Alkylengruppe mit 1 bis 20 Kohlenstoffatomen bedeuten.

2. Polymer nach Anspruch 1, in welchem die Gruppen Ar<sup>1</sup>, Ar<sup>2</sup>, Ar<sup>3</sup> und Ar<sup>4</sup> jeweils ausgewählt sind aus

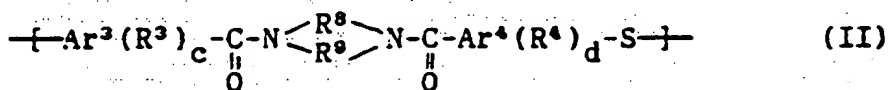
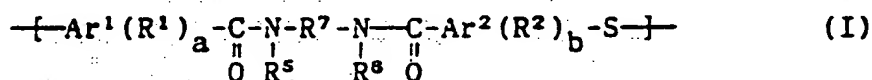


worin Z -O-, -S-, -SO<sub>2</sub>-, -CO-, -CH<sub>2</sub>- oder -C(CH<sub>3</sub>)<sub>2</sub>- bedeutet.

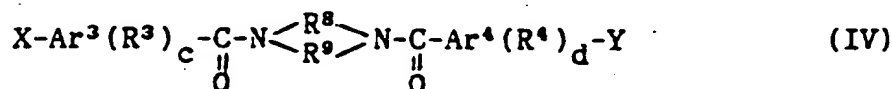
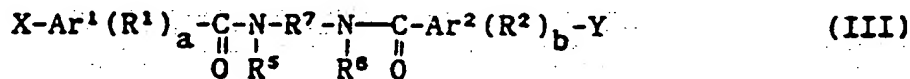
3. Polymer nach Anspruch 1 oder Anspruch 2, welches eine logarithmische Viskosität  $[\eta]$  von 0,02 bis 2,00, vorzugsweise 0,05 bis 2,0 hat, bestimmt durch Messen der relativen Viskosität des in konzentrierter Schwefelsäure gelösten Polymers bei 30°C und bei einer Polymerkonzentration von 0,5 g/100 ml und Berechnen des Ergebnisses gemäß der Gleichung:

$$[\eta] = \ln \frac{(\text{relative Viskosität})}{(\text{Polymerkonzentration})}$$

4. Polymer nach den Ansprüchen 1 bis 3, welches durch Erwärmen in einer oxidierenden Atmosphäre kettenverlängert und/oder vernetzt und/oder verzweigt worden ist.
5. Verfahren zur Herstellung eines aromatischen Sulfid-Amid-Polymers, welches wiederkehrende Einheiten umfaßt, die durch die folgende Formel (I) und/oder (II) dargestellt sind:



wobei das Verfahren den Schritt des Sulfidierens von einer oder mehreren Amidgruppen enthaltenden Dihalogenidverbindungen mit der folgenden allgemeinen Formel (III) und/oder (IV) mit einem sulfidierenden Mittel in einem organischen polaren Lösungsmittel umfaßt:



worin Ar<sup>1</sup>, Ar<sup>2</sup>, Ar<sup>3</sup> und Ar<sup>4</sup> jeweils einen aromatischen Ring bedeuten; R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup>, R<sup>4</sup>, R<sup>5</sup> und R<sup>6</sup>, die

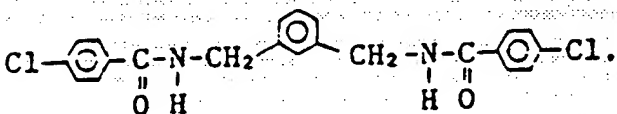
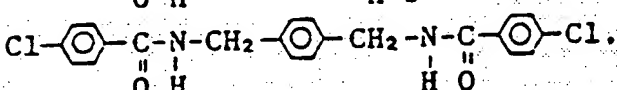
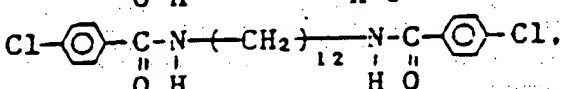
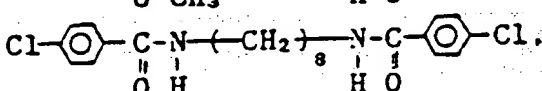
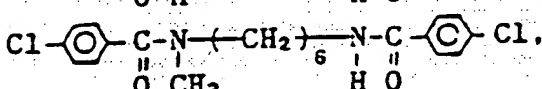
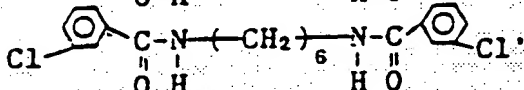
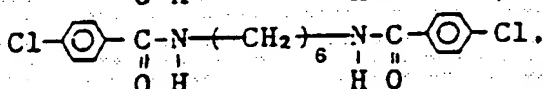
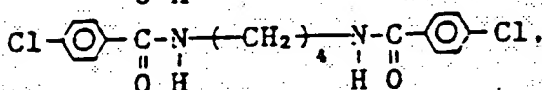
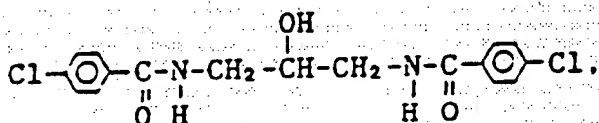
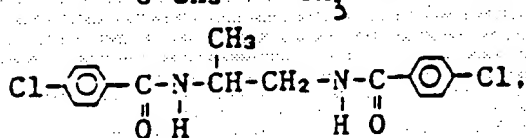
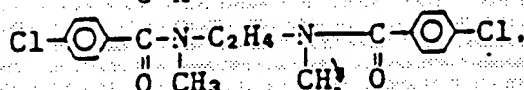
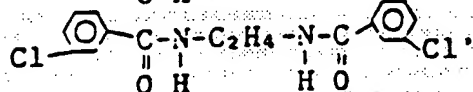
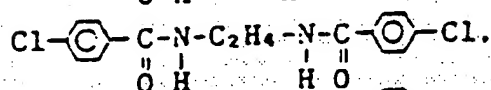
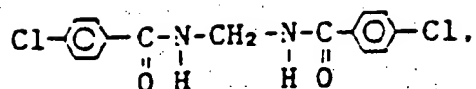
gleich oder voneinander verschieden sein können, jeweils eine Alkylgruppe mit 1 bis 20 Kohlenstoffatomen, eine Cycloalkylgruppe mit 3 bis 20 Kohlenstoffatomen, eine Arylgruppe mit 6 bis 20 Kohlenstoffatomen, eine Alkoxygruppe mit 1 bis 20 Kohlenstoffatomen, eine Acylgruppe mit 2 bis 20 Kohlenstoffatomen oder eine Arylalkylgruppe mit 7 bis 20 Kohlenstoffatomen bedeuten, wobei  $R^5$  und  $R^6$  jeweils wahlweise Wasserstoff sind; a, b, c und d, die gleich oder voneinander verschieden sein können, jeweils eine ganze Zahl von 0 bis 4 bedeuten;  $R^7$ ,  $R^8$  und  $R^9$ , die gleich oder voneinander verschieden sein können, jeweils eine Alkylengruppe mit 1 bis 20 Kohlenstoffatomen bedeuten; und X und Y, die gleich oder voneinander verschieden sein können, jeweils ein Halogen bedeuten.

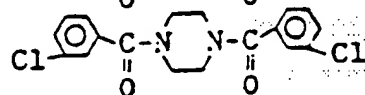
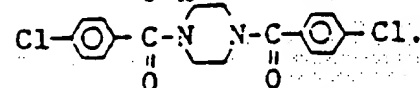
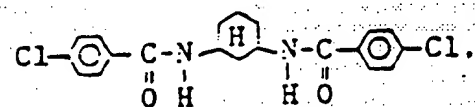
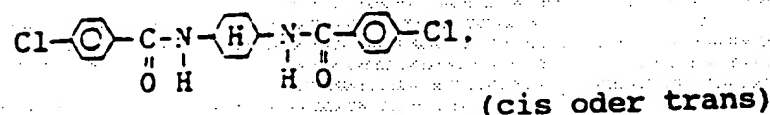
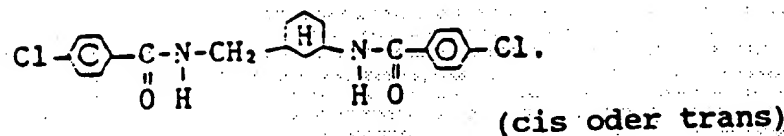
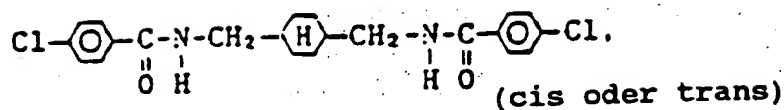
6. Verfahren nach Anspruch 5, in welchem die Gruppen  $Ar^1$ ,  $Ar^2$ ,  $Ar^3$  und  $Ar^4$  jeweils ausgewählt sind aus



worin Z -O-, -S-, -SO<sub>2</sub>-, -CO-, -CH<sub>2</sub>- oder -C(CH<sub>3</sub>)<sub>2</sub>- bedeutet.

7. Verfahren nach Anspruch 5 oder Anspruch 6, in welchem die eingesetzte Amidgruppen enthaltende Dihalogenidverbindung ausgewählt ist aus der Gruppe bestehend aus:



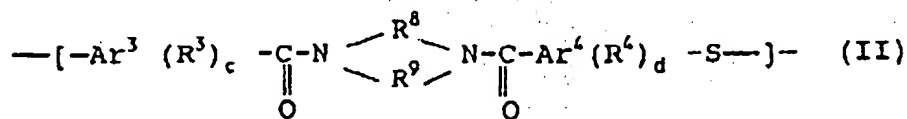
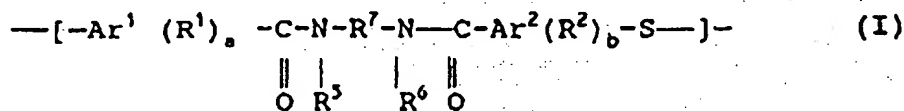


und Mischungen davon.

8. Verfahren nach Anspruch 5, 6 oder 7, in welchem das organische Lösungsmittel aprotisch ist.
9. Verfahren nach Anspruch 8, in welchem das Lösungsmittel ausgewählt ist aus N,N-Dimethylacetamid, N-Ethyl-2-pyrrolidon, Hexamethylphosphorsäuretriamid, Dimethylsulfoxid, N-Methyl-2-pyrrolidon und 1,3-Dimethylimidazolin.
10. Verfahren nach Anspruch 5, 6, 7, 8 oder 9, in welchem das sulfidierende Mittel ausgewählt ist aus Natriumsulfid, einer Kombination aus Natriumhydrogensulfid und Natriumhydroxid und einer Kombination aus Schwefelwasserstoff und Natriumhydroxid.
11. Zusammensetzung, die ein aromatisches Sulfid-Amid-Polymer, das in Anspruch 1, 2, 3 oder 4 beansprucht ist, oder durch ein Verfahren hergestellt ist, das in einem der Ansprüche 5 bis 10 beansprucht ist, und ein oder mehrere herkömmliche Additive umfaßt.

#### Revendications

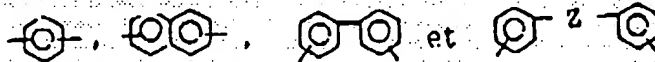
1. Polymère de sulfure-amide aromatique qui comprend les motifs de base représentés par les formules suivantes (I) et/ou (II) :



dans lesquelles  $\text{Ar}^1$ ,  $\text{Ar}^2$ ,  $\text{Ar}^3$  et  $\text{Ar}^4$  représentent chacun un noyau aromatique;  $\text{R}^1$ ,  $\text{R}^2$ ,  $\text{R}^3$ ,  $\text{R}^4$ ,  $\text{R}^5$  et  $\text{R}^6$ , qui peuvent être identiques ou différents, représentent chacun un groupe alkyle ayant 1 à 20 atomes

de carbone, un groupe cycloalkyle ayant 3 à 20 atomes de carbone, un groupe aryle ayant 6 à 20 atomes de carbone, un groupe alcoxy ayant 1 à 20 atomes de carbone, un groupe acyle ayant 2 à 20 atomes de carbone et un groupe arylalkyle ayant 7 à 20 atomes de carbone, chacun des groupes R<sup>5</sup> et R<sup>6</sup> étant éventuellement de l'hydrogène; a, b, c et d, qui peuvent être identiques ou différents, représentent chacun un nombre entier de 0 à 4; et R<sup>7</sup>, R<sup>8</sup> et R<sup>9</sup>, qui peuvent être identiques ou différents, représentent chacun un groupe alkylène ayant 1 à 20 atomes de carbone.

2. Polymère selon la revendication 1, dans lequel les groupes Ar<sup>1</sup>, Ar<sup>2</sup>, Ar<sup>3</sup> et Ar<sup>4</sup> sont chacun choisis parmi les suivants :

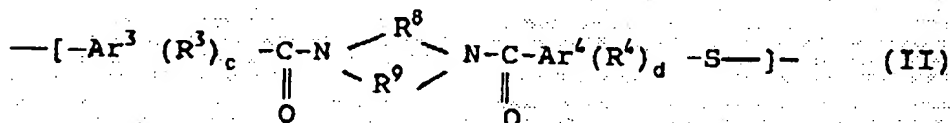
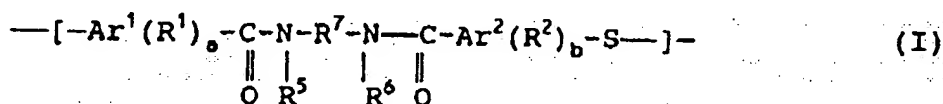


où Z représente -O-, -S-, -SO<sub>2</sub>-, -CO-, -CH<sub>2</sub>- ou -C(CH<sub>3</sub>)<sub>2</sub>-.

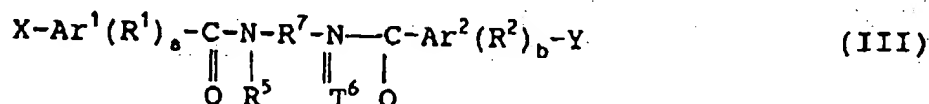
3. Polymère selon la revendication 1 ou 2 qui a une viscosité logarithmique  $[\eta]$  de 0,02 à 2,00, de préférence de 0,05 à 2,0, comme déterminé par la mesure de la viscosité relative du polymère dissous dans de l'acide sulfurique concentré à 30 °C et selon une concentration du polymère de 0,5 g/100 ml et par le calcul du résultat selon l'équation suivante :

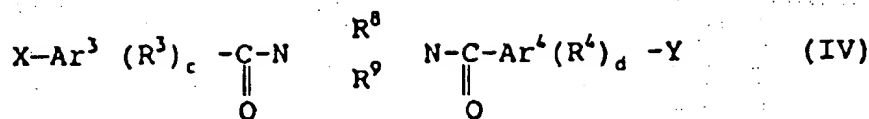
$$[\eta] = \ln \frac{(\text{viscosité relative})}{(\text{concentration du polymère})}$$

4. Polymère selon les revendications 1 à 3, qui est soumis à une extension de chaîne et/ou à une réticulation et/ou à une ramification par chauffage dans une atmosphère oxydante.
5. Procédé de production d'un polymère de sulfure-amide aromatique qui comprend les motifs de base représentés par les formules suivantes (I) et/ou (II) :



ledit procédé consistant à sulfurer un ou plusieurs composés dihalogénés contenant un ou plusieurs groupes amide ayant la formule générale suivante (III) et/ou (IV) avec un agent de sulfuration dans un solvant polaire organique :





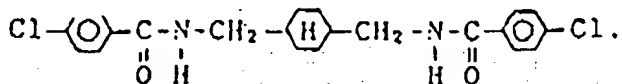
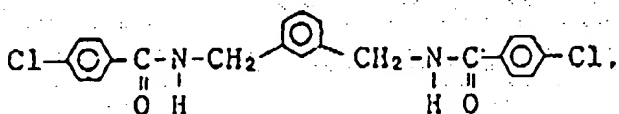
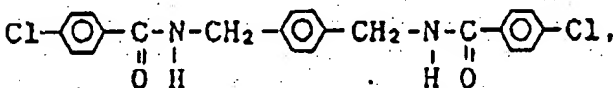
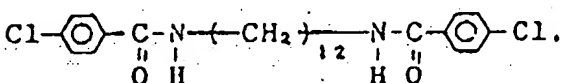
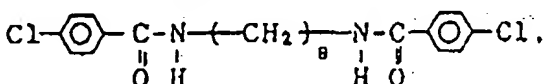
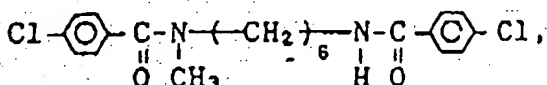
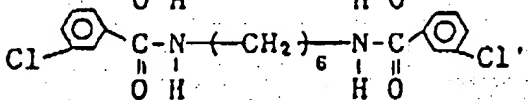
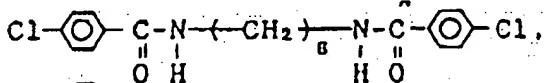
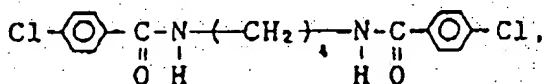
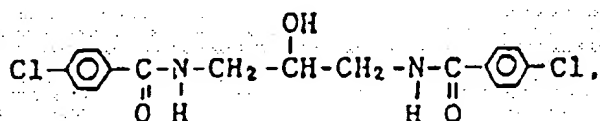
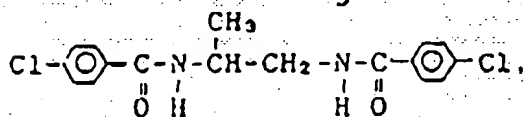
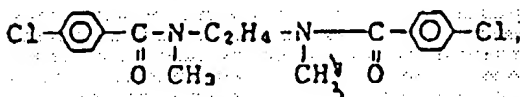
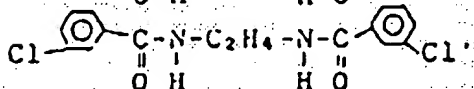
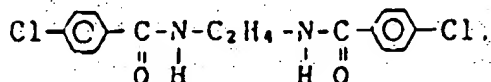
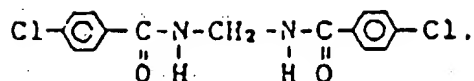
dans lesquelles  $Ar^1$ ,  $Ar^2$ ,  $Ar^3$ , et  $Ar^4$  représentent chacun un noyau aromatique;  $R^1$ ,  $R^2$ ,  $R^3$ ,  $R^4$ ,  $R^5$  et  $R^6$ , qui peuvent être identiques ou différents, représentent chacun un groupe alkyle ayant 1 à 20 atomes de carbone, un groupe cycloalkyle ayant 3 à 20 atomes de carbone, un groupe aryle ayant 6 à 20 atomes de carbone, un groupe alcoxy ayant 1 à 20 atomes de carbone, un groupe acyle ayant 2 à 20 atomes de carbone et un groupe arylalkyle ayant 7 à 20 atomes de carbone, chacun des groupes  $R^5$  et  $R^6$  étant éventuellement de l'hydrogène; a, b, c et d, qui peuvent être identiques ou différents, représentent chacun un nombre entier de 0 à 4; et  $R^7$ ,  $R^8$  et  $R^9$ , qui peuvent être identiques ou différents, représentent chacun un groupe alkylène ayant 1 à 20 atomes de carbone; et X et Y, qui peuvent être identiques ou différents, représentent chacun un halogène.

6. Procédé selon la revendication 5, dans lequel les groupes  $Ar^1$ ,  $Ar^2$ ,  $Ar^3$  et  $Ar^4$  sont chacun choisi parmi les suivants :



où Z représente  $-O-$ ,  $-S-$ ,  $-SO_2-$ ,  $-CO-$ ,  $-CH_2-$  ou  $-C(CH_3)_2-$ .

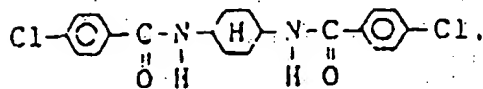
7. Procédé selon la revendication 5 ou 6, dans lequel le composé dihalogéné contenant des groupes amide est choisi parmi les groupes suivants :



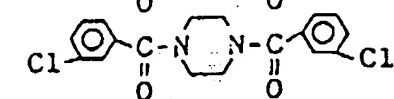
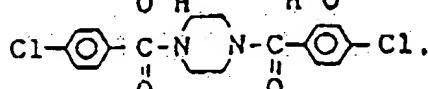
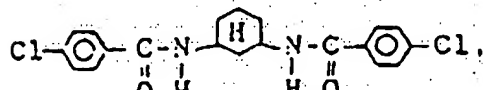
(cis. ou trans)



(cis ou trans)



(cis ou trans)



et leurs mélanges.

8. Procédé selon la revendication 5, 6 ou 7 dans lequel le solvant organique est aprotique.

9. Procédé selon la revendication 8, dans lequel le solvant est choisi parmi le N,N-diméthyl acétamide (DMA), la N-éthyl-2-pyrrolidone, le hexaméthyl phosphoramide (HMPA), le diméthyl sulfoxyde (DMSO), la N-méthyl-2-pyrrolidone (NMP) et la 1,3-diméthyl imidazoline.

10. Procédé selon la revendication 5, 6, 7, 8 ou 9, dans lequel l'agent de sulfuration est choisi parmi le sulfure de sodium, une combinaison d'hydrosulfure de sodium et d'hydroxyde de sodium, et une combinaison de sulfure d'hydrogène et d'hydroxyde de sodium.

11. Composition comprenant un polymère de sulfure-amide aromatique selon la revendication 1, 2, 3 ou 4 ou produit par un procédé selon l'une quelconque des revendications 5 à 10 et un ou plusieurs additifs conventionnels.

Fig. 1

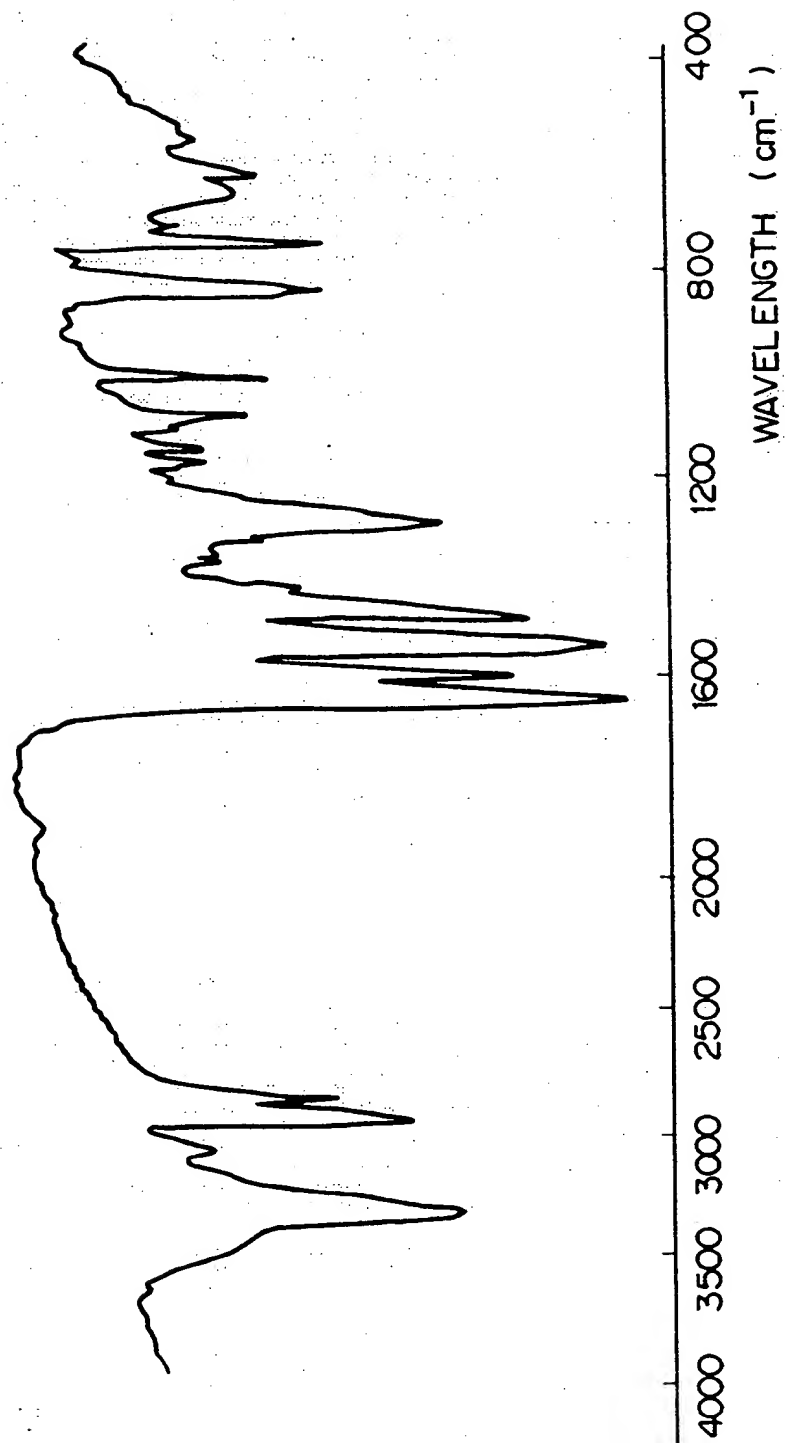


Fig. 2

